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SYNTHESIS AND CHARACTERIZATION OF METALLO-ORGANIC CONDUCTING MA--ETC(U)

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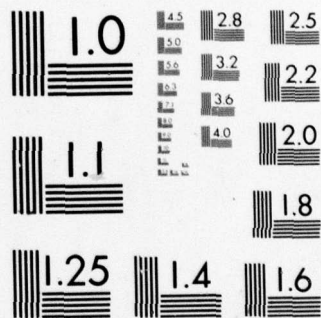
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Synthesis and Characterization of Metallo-organic
Conducting Materials with Tetraazaannulenes

by

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Compounds of the macrocyclic ligand [4,11-dihydro-dibenzo[b,1][1,4,8,11]tetraaza-[14]annulene, dB-TAA, have been prepared with Cu ²⁺ , Ni ²⁺ , Co ²⁺ , Pd ²⁺ , Pt ²⁺ . The palladium complex crystallizes in two crystalline modifications, one of which is similar to the structurally characterized compound Ni(dB-TAA), while the second form packs as cofacial dimers in the solid state. Partial oxidation of Pd(dB-TAA) and Pt(dB-TAA) yields the mixed valence nonstoichiometric compounds Pd(dB-TAA)I _{2.0} ($\sigma = 0.4 \text{ ohm}^{-1}\text{cm}^{-1}$, $\Delta E = 0.04\text{--}0.06 \text{ eV}$), Pt(dB-TAA)I _{1.35} ($\sigma = 0.12 \text{ ohm}^{-1}\text{cm}^{-1}$, $\Delta E = 0.06\text{--}0.12 \text{ eV}$), and Pt(dB-TAA)I _{1.50} ($\sigma = 0.03 \text{ ohm}^{-1}\text{cm}^{-1}$).		

Synthesis and Characterization of Metallo-organic Conducting Materials with Tetraazaannulenes

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Intensive research activities in university, industrial and national research laboratories on mixed valence organic and metallo-organic compounds have led to insights into the chemical and structural features which determine such physical properties as magnetic behavior and electrical conductivities.¹ The aim of the research is the production of new materials with properties which may be exploited in technological applications, with the expected dividends being the discovery of new phenomena, the invention of new experimental methods, and the development of new theoretical models. The recent observation² of superconductivity in bis(tetramethyltetraselenafulvalene)hexafluorophosphate, (TMTSF)₂PF₆, provides an excellent example of the successes which may be expected as this research area is expanded and developed.

This paper presents a brief survey of research on mixed valence tetraazaannulene complexes which is underway in our laboratory. As noted in the reference citations much of this work is being carried out in collaboration with research groups at the University of North Carolina and elsewhere. The systems to be discussed include a series of macrocyclic tetraazaannulene complexes with Cu²⁺, Ni²⁺, Co²⁺, Pd²⁺, and Pt²⁺ and their partially oxidized reaction products. As will be shown the electrical conductivities and activation energies of some of these compounds approach those of the partially oxidized metallo-phthalocyanines which exhibit metal-like temperature dependencies of σ , and of the partially oxidized metalloporphyrins.³

An X-ray structural study⁴ has shown that the nickel complex of the ligand (4,11-dihydro-dibenzo[b,i][1,4,8,11]tetraaza[14]annulene Ni(dB-TAA), is essentially planar, and that the molecules pack in slipped stacks in the solid state. Even though the slipped nature of the stacks results in a long nickel-nickel distance in adjacent molecules of 5.228 Å, the interplanar separations between crystallographically inequivalent molecules are 3.235 and 3.295 Å. These distances are slightly shorter than the 3.35 Å interplanar separation in graphite and permit extensive π - π interactions between adjacent molecules, thus making partially oxidized analogues good candidates for systematic studies of structural and chemical effects on electrical conductivities.

Synthetic Procedure

Complexes of copper(II), nickel(II), cobalt(II), palladium(II), and platinum(II) with the tetraazaannulene were prepared⁵ in good yield by an initial reaction of a metal salt (the acetate in the case of copper(II), nickel(II), and cobalt(II); K₂PdCl₄; or K₂PtCl₄) with o-phenylenediamine in ethylene glycol, followed by addition of Na⁺C₃H₃O₂⁻. The reaction mixtures thus obtained were stirred at reflux for 5 hours, cooled to room temperature, and the products collected by filtration. The crude products were washed with ethanol, acetone, and diethyl ether, and air dried. Highly purified samples were obtained by vacuum sublimation (350°C; 0.005 mm Hg). Analytical data for carbon, hydrogen, and nitrogen on the metallocycles differed from the calculated values by less than 0.03% in all cases.

X-ray crystallographic studies have revealed that there are two crystalline forms of Pd(dB-TAA).⁶ One of these, designated α -Pd(dB-TAA), which was obtained by vacuum sublimation of the crude reaction product crystallizes in the monoclinic system with $a = 19.426(23)$, $b = 5.292(7)$, $c = 14.838(3)$, and $\beta = 112.32(8)$. Based on the similarity in the structural data for α -Pd(dB-TAA) and Ni(dB-TAA) which is summarized in Table I, it is reasonable to conclude that the two compounds are isostructural, with planar α -Pd(dB-TAA) molecules stacking in a slipped fashion.

A second crystalline form of the palladium compound, β -Pd(dB-TAA), was obtained from the batch of crystals which yielded α -Pd(dB-TAA). The structure

Table I. Unit Cell Data for Ni(dB-TAA and α -Pd(dB-TAA)

Compound	a , Å	b , Å	c , Å	β , deg
Ni(dB-TAA) ^a	19.456(4)	5.228(1)	14.868(3)	112.28(1)
α -Pd(dB-TAA) ^b	19.426(23)	5.292(7)	14.838(3)	112.32(8)

^a Reference 4.

^b Reference 6.

of β -Pd(dB-TAA) is currently under study by X-ray crystallography. Some important molecular dimensions at the present level of refinement [$R(\text{anisotropic}) = 4.1\%$], are given in Table II. The material crystallizes in the monoclinic system, space group $P2_1/c$ with four molecules in a unit cell of dimensions $a = 8.974(8)$, $b = 10.985(10)$, $c = 14.617(10)$, and $\beta = 95.14(9)$. Although all atoms sit on general positions, the molecule is very nearly planar, with the largest deviation from the best least squares plane for all non-hydrogen atoms being $0.047(0.010)$ Å for an apical carbon (C11) of one of the propane-1,3-diiminato exocyclic rings. The palladium atom lies at $-0.035(0.001)$ Å with respect to this plane. In a similar calculation, the palladium atom sits at $-0.016(0.001)$ Å from the best least squares plane formed by the four nitrogen donor atoms.

As shown in Figure 1, the packing of the molecules in the solid state is distinctly different from that exhibited by the nickel analogue. Instead of the slipped molecular stacking as occurs in Ni(dB-TAA), the molecules of β -Pd(dB-TAA) are arranged in pairs. The shortest palladium-palladium distance is $4.382(1)$ Å, with the next shortest distance between palladium atoms in adjacent pairs being 6.643 Å. The closest contact of the palladium ion with an adjacent molecule of a given pair is to C9 with Pd-C9' being $3.432(4)$ Å. Other close contacts are Pd-N2' of $4.178(4)$ Å and Pd-N3' of $3.645(4)$ Å. The Pd-C9'-Pd' angle is $88.02(11)^\circ$.

The average bond distance in the C4-C9 benzenoid ring is 1.390 Å, and the average angle in the ring is 120.0° . The comparable average bond distance and angle in the C13-C18 ring is 1.397 Å and 120.0° . The inter-nuclear distances between the nitrogen donor atoms in the coordination plane are

N1-N2	$2.915(5)$ Å
N1-N4	$2.609(5)$ Å
N2-N3	$2.605(5)$ Å
N3-N4	$2.938(5)$ Å

Efforts to obtain crystals by deposition from an appropriate solvent are underway.

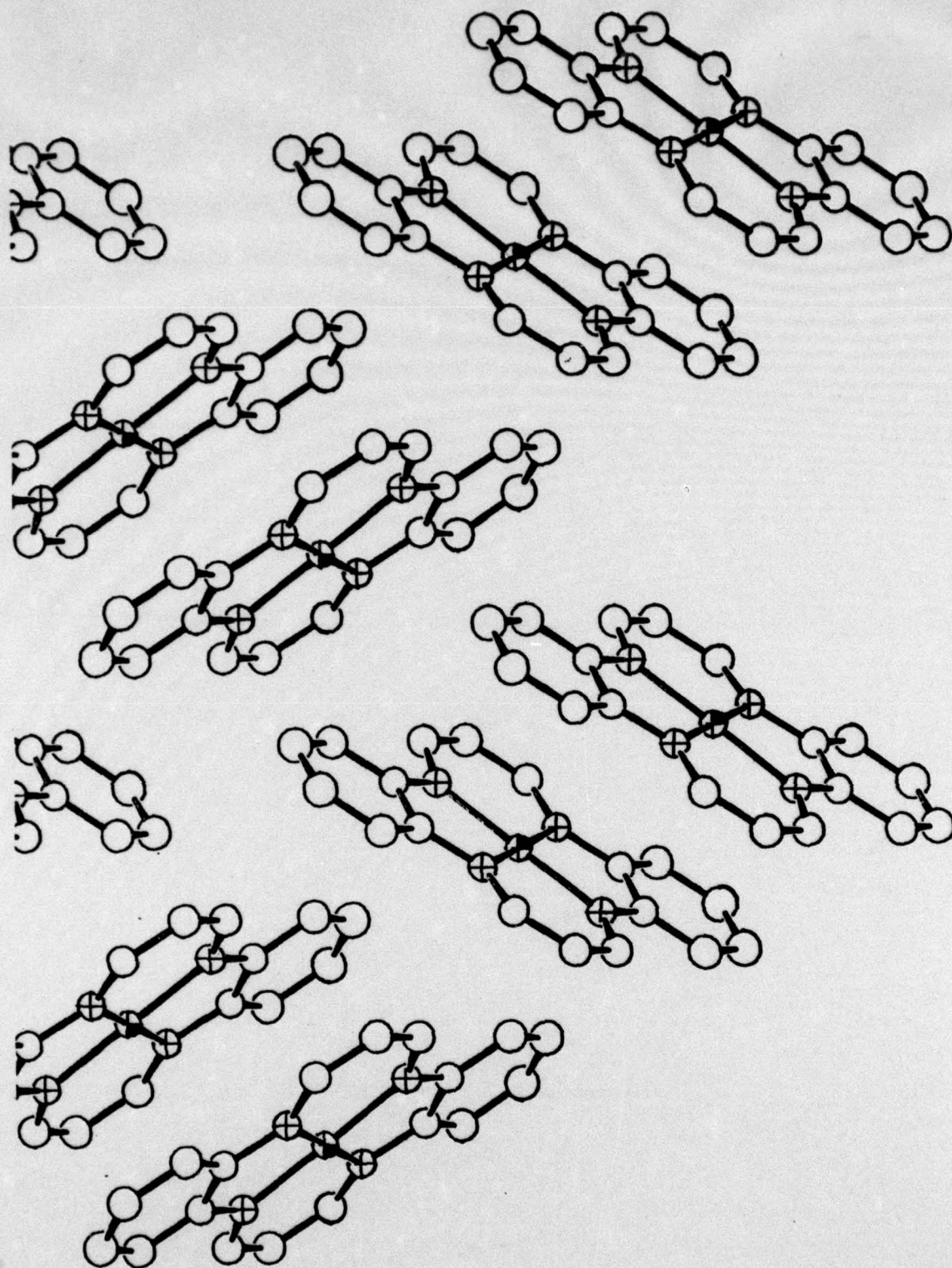
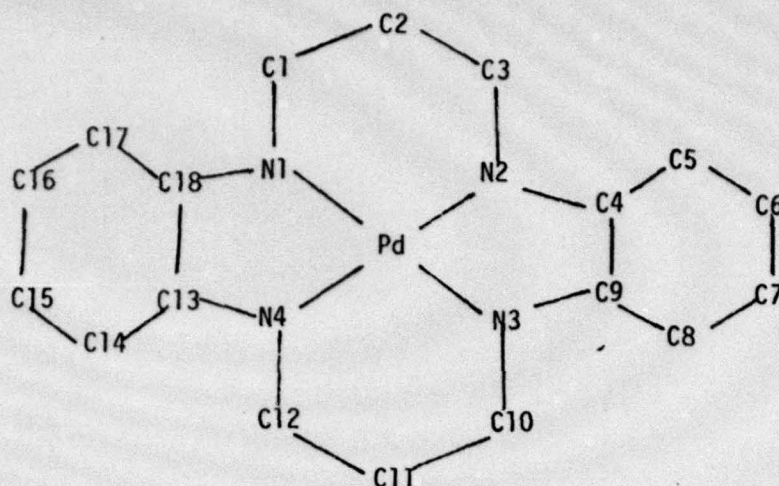


Figure 1. A view of several β -Pd(dB-TAA) molecules projected on the bc plane which shows the formation of cofacial dimers and the packing of the dimers.

Table II. Selected Bond Distances and Angles for β -Pd(dB-TAA).Bond Lengths

Pd-N1	1.954(4)
Pd-N2	1.951(4)
Pd-N3	1.967(4)
Pd-N4	1.963(4)
N1-C1	1.323(6)
N1-C18	1.421(6)
C1-C2	1.384(7)
C2-C3	1.386(7)
N2-C3	1.327(6)
N2-C4	1.427(5)
N3-C9	1.417(6)
N3-C10	1.319(6)
C10-C11	1.390(7)
C11-C12	1.398(7)
N4-C12	1.310(5)
N4-C13	1.414(5)

Bond Angles

N1-Pd-N2	96.41(15)
N2-Pd-N3	83.37(15)
N3-Pd-N4	96.80(15)
N4-Pd-N1	83.41(15)
Pd-N1-C1	122.23(32)
Pd-N1-C18	113.53(28)
Pd-N2-C3	122.99(32)
Pd-N2-C4	113.21(28)
Pd-N3-C9	113.46(28)
Pd-N3-C10	121.71(32)
Pd-N4-C12	122.80(32)
Pd-N4-C13	113.36(29)
C1-C2-C3	128.21(44)
C10-C11-C12	128.61(43)

Oxidation with Iodine

After refluxing for 16 hours in chlorobenzene in the presence of an initial ten-fold excess of iodine, Pd(dB-TAA) yields Pd(dB-TAA)I_{2.0}. The mixed valence compounds Pt(dB-TAA)I_{1.35} and Pt(dB-TAA)I_{1.5} result from heating Pt(dB-TAA) in 1,2,4-trichlorobenzene at 200°C in the presence of a ten-fold excess of iodine for 16 and 24 hours, respectively. The resonance Raman spectra of these materials using 488 nm excitation exhibited bands at 105-115 cm⁻¹ with overtones near 210 cm⁻¹, values which are consistent with the presence of polyiodide counterions. Attempts to obtain single crystals for structural and conductivity studies are underway.

Electrical Conductivities

Electrical conductivities of pressed pellet samples were determined by a four probe d.c. method using the van der Pauw technique. The pellets, which were 1.3 cm in diameter and approximately 0.2 cm thick, were compacted using a Beckman KBr die and a ring press operated routinely at ten tons of pressure. A Keithley Model 227 which was operated typically at 10 μ amp and a Keithley Model 180 nanavoltmeter were used to measure the electrical conduction properties. Electrical contacts were made with silver paste. Pellets which did not provide ohmic characteristics were rejected. Activation

energies were determined from temperature variation studies of the electrical conductivities in the range 77 to 300 K using a glass Dewar equipped with a sample holder which was fitted with resistance heater and temperature sensors. Temperatures were measured with a calibrated platinum resistance thermometer. Measurements were made in an isothermal mode provided by the resistance heater, radiation heat leak to the cryogen, and a Lake Shore Cryotronics Model DTC-500 temperature controller. Room temperature conductivities and activation energies, where available, are summarized in Table III where it may be seen that partial oxidation of the macrocyclic complexes leads to a great enhancement of the electrical conductivities of the materials.

Table III. Electrical Conductivities and Activation Energies for $M(\text{TAA})\text{I}_x$.

Compound	σ , $\text{ohm}^{-1} \text{cm}^{-1}$ (R.T.)	ΔE , eV
Cu(dB-TAA)	$<10^{-8}$	
Ni(dB-TAA)	$<10^{-8}$	
Co(dB-TAA)	$<10^{-8}$	
Pb(dB-TAA)	$\sim 10^{-8}$	
Pt(dB-TAA)	$\sim 10^{-8}$	
Pd(dB-TAA) $\text{I}_{2.0}$	0.4	0.04-0.06
Pt(dB-TAA) $\text{I}_{1.35}$	0.12	0.06-0.12
Pt(dB-TAA) $\text{I}_{1.50}$	0.03	

Concluding Statements

Since it is well known that electrical conductivities of pressed pellets are considerably smaller than the intrinsic conductivities of the materials because of contributions to the resistivity from interparticle contact resistances and because of the inherent anisotropy of low-dimensional systems, there is considerable stimulation for continued efforts to obtain single crystal samples of $M(\text{TAA})\text{I}_x$. It is likely that such single crystals will exhibit metal-like conductivities i.e. $d\sigma/dT < 0$, since the conductivities and activation energies of pressed pellet samples of these materials are comparable to those observed for $\text{Ni}(\text{phthalocyanine})(\text{I}_3)_{0.3}$, a substance known to exhibit metal-like conductivity.^{3b}

The relatively long palladium-palladium distances in the stacked and dimeric forms of Pd(dB-TAA) leads to the conclusion that metal-metal interactions do not contribute significantly to any band formation, and that intermolecular interactions occur between the π -orbitals of partially oxidized macrocyclic complexes.

Acknowledgments

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